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Odor development in refined meadowfoam (*Limnanthes alba*) oil

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Abstract

Meadowfoam (*Limanthes alba*) is an alternative oilseed crop that has application in personal care products. Offensive odor development in refined meadowfoam oil can be a problem for processors and formulators. To identify possible sources of the odor, the headspace above refined and deodorized meadowfoam oils was examined. Compound analyses were based on solid-phase microextraction (SPME) and Gas chromatography-mass spectroscopy (GC–MS) techniques. Hexanal, heptanal, octanal, and nonanal were detected in the headspace of malodorous samples. Nonanal was also detected in the headspace of non-malodorous meadowfoam oil after a 4 week period at 60 °C.

Keywords: Meadowfoam; *Limnanthes alba*; Malodor; Headspace analysis

1. Introduction

Meadowfoam (*Limnanthes alba*) is an emerging oilseed crop cultivated in the United States. The oil typically contains 65% C20:1 and 20% C22:1 fatty acids (Princen, 1983; Princen and Rothfus, 1984). Meadowfoam oil and related derivatives are currently used in numerous personal-care products. The oil is produced commercially by solvent extraction of conditioned and flaked seed. The crude oil is refined and deodorized by conventional processes. The development of offensive odors in the processed oil is undesirable for its intended uses.

Studies on the effects of processing and storage conditions on the development of off-flavors in edible oils have shown that oxidative and hydrolytic mechanisms can degrade these oils to compounds that reduce the quality of the oil to organoleptically unacceptable levels (Gomes and Caponio, 1998; Kao et al., 1998). Oils composed of saturated fatty acids are more stable to oxidation than unsaturated fatty acids that can oxidize rapidly at atmospheric conditions. Oxidation of the allylic methylene structure of the unsaturated fatty acid is the potential site for the initiation of degradative processes.

Meadowfoam oil contains a high degree of

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unsaturation and yet exhibits high oxidative stability compared to other seed oils. This stability, however, decreases as antioxidants are removed during the refining process. Subsequent exposure of the refined oil to elevated temperatures could promote the formation of oxidation products, and thereby decrease oil quality (Gavin, 1991).

Additionally, meadowfoam seeds contain glucosinolate, glucolimnanthin, which may hydrolyze to form volatile compounds, for example, 3-methoxyphenyl acetonitrile and 3-methoxybenzyl isothiocyanate (Vaughn et al., 1996). Seed that is conditioned at elevated temperature and moisture levels prior to flaking does not form these compounds because the enzyme responsible for glucosinolate degradation is inactivated (Carlson et al., 1998). This produces both higher quality oil and meal.

The purpose of this study was to identify volatile compounds present in refined and deodorized meadowfoam oils. The headspace was sampled with solid-phase microextraction (SPME) and analyzed by mass spectrometric techniques. Identification of compounds in the headspace could indicate the origin and possible mechanism responsible for the development of malodors in meadowfoam oils.

2. Materials and methods

2.1. Meadowfoam oil

Meadowfoam oil was obtained from Fanning Corp. (Chicago, IL). The oil was produced commercially by hexane extraction of conditioned and flaked meadowfoam seed. The crude oil was filtered, caustic refined, and steam deodorized prior to storage. All samples tested were taken from the same product batch, but from different storage containers. These samples included an acceptable product set and a product set that had developed malodors and were deemed unacceptable. Each set consisted of three samples taken from corresponding containers.

2.2. Analytical

Headspace analysis was performed by SPME using a 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) fiber (Supelco, Bellefonte, PA). A 0.5 ml aliquot of the oil sample was placed into a 2 ml screw-cap vial fitted with a polytetrafluorinated ethylene (PTFE) septum. The fiber was inserted through the septum and the fiber equilibrated in the headspace for 2 h at 25 °C. Analyses were performed with the HP-5890 Series II Plus Gas Chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with a Model 5972 Mass Selective detector. The front injection port of the instrument was fitted with a low-volume liner, and the instrument was set for splitless injection. A 30 m × 0.2 mm diameter SPB-1 capillary column (Supelco) was used with a temperature program of 35–150 °C at 5 °C/min and 150–250 °C at 20 °C/min. The detector was set to scan the range of 40–550 amu. The fiber was inserted into the 250 °C injection port for 1 min to desorb the sample. The fiber was then removed from the injection port and conditioned at 250 °C for 1 h to prepare for the next analysis. Sample spectra were identified by comparison with standards (Sigma-Aldrich Chemicals, St. Louis, MO). All analyses were run in duplicate.

2.3. Accelerated storage

Samples from the acceptable product set of meadowfoam oil were stored at elevated temperature and sampled periodically to follow the development and accumulation of volatile compounds in the headspace of these oils. 12 sample vials were prepared containing 1 ml aliquots of oil in 2 ml glass screw-cap vials with PTFE-lined septa caps and stored in a laboratory oven controlled at 60 °C for 6 weeks. At weekly intervals, two vials were removed and submitted to headspace analysis. Headspace sampling was performed by removing a vial from the oven and inserting the SPME fiber through the septum. The fiber was exposed to the headspace for 15 min. Additional oil samples

were prepared and stored at −5 and 25 °C conditions for comparison.

3. Results and discussion

The presence of hexanal, heptanal, octanal, and nonanal was identified in the headspace of the malodorous sample (Table 1). These compounds are consistent with the oxidative degradation of fatty acids and have been correlated with the development and occurrence of off-flavors in edible oils (Shahidi et al., 1997; Jelen et al., 2000). Headspace analysis of oil samples taken from the acceptable product set and the commercially re-deodorized product set did not have these aldehydes.

The formation of these compounds most probably occurred during storage because the steam deodorization process would have removed such organic compounds. The deodorization process can have a profound effect on the quality of vegetable oils (Maza et al., 1992; Kao et al., 1998). The typical operation of a commercial deodorizer holds the material above 250 °C under vacuum with a steam or nitrogen sparge. This elevated temperature can also promote the degradation of triglycerides because the natural antioxidants have been removed at this stage of processing. However, as deodorization is performed under vacuum, any volatile compounds generated in the process are also removed from the product.

To complement the headspace analysis of the malodorous meadowfoam oil samples, a set of acceptable meadowfoam oil samples was subjected to a period of storage at a constant temperature of 60 °C. By the 4th week of storage, the headspace of these samples contained detectable levels of nonanal, decanal, dodecanal, and 9,12-octadecadienoic acid. Duplicate samples stored at −5 and 25 °C conditions did not contain detectable levels of these volatile compounds. Such results indicate that volatile compounds can form in the headspace

Table 1
Headspace components of malodorous meadowfoam oil samples

Retention time (min)	Relative intensity[a]	Fragment ions (amu)	Compound	Concentration[b] (ppb)
5.7	42,000	41 44 56 72	Hexanal	130 ± 7
9.7	12,000	41 44 57 70 81	Heptanal	33 ± 2
13.5	63,000	41 43 57 69 81 100	Octanal	90 ± 5
17	273,000	41 44 57 70 81 98 114	Nonanal	260 ± 13

[a] Total ion concentration.
[b] Average of replicates, $N = 3$.

of refined and deodorized meadowfoam oil within a relatively short period at moderately elevated temperature.

The autoxidation of unsaturated triglycerides is believed to proceed through a free radical mechanism, leading to the fragmentation and rearrangement of the starting material to produce a mixture of acids, aldehydes, and alcohols (Frankel, 1998). A complex series of reactions exists, and a particular fatty acid can generate numerous degradation products from the initial hydroperoxide. While it is not possible to predict the distribution of degradation products for a specific triglyceride, aldehydes have been detected in the headspace of several vegetable oils containing unsaturated fatty acids, e.g. oleic, linoleic, and linolenic, subjected to elevated storage temperatures (Jelen et al., 2000). These results are consistent with the oxidative process of hydroperoxide formation and scission that occur at the unsaturated sites of fatty acids.

The expected glucosinolate degradation compounds were not detected in any of the oil headspace samples tested. Glucosinolate, glucolimnanthin, is known to produce a variety of thiocyanate and isothiocyanate degradation compounds, depending on the prevailing conditions (Bartelt and Mikolajczak, 1989; Vaughn et al., 1996). The absence of these materials indicates that the seed conditioning performed at the processing facility was effective in deactivating the enzyme responsible for initiating degradation or that the deodorization process was effective in removing the degradation compounds.

4. Conclusions

Compounds that could contribute to odor development during storage were identified by GC–MS–SPME headspace analysis of commercially refined and deodorized meadowfoam oil. Detectable amounts of hexanal, heptanal, octanal, and nonanal were present. Individually, and at relatively low concentrations, these compounds can elicit a strong olfactory response and when reacting synergistically could further provoke an increased negative organoleptic response at very low levels.

The aldehyde compounds could be degradation products of the unsaturated meadowfoam fatty acids. The distribution of aldehydes detected in the headspace of commercial meadowfoam oil stored at elevated temperature in the laboratory differed from that measured in the malodorous commercially processed oils. For example, nonanal was detected in the re-deodorized sample, whereas the shorter chain aldehydes were not. Variable storage conditions are assumed to affect the degradation pathway and the distribution and accumulation of volatile compounds.

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